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OF DENSE CLOUDS
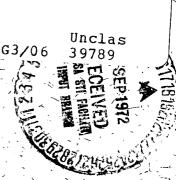
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I. ASTRONOMICAL PROBLEM

The origin and subsequent evolution of the complex array of molecules found in dense, heavily obscured clouds present a variety of significant astronomical and chemical problems. Several investigations, e. g., the Liege Symposium, Stellar Evolution Before the Main Sequence, (197); Kaplan and Pikelner, (1970); and recent papers by Cameron (1969, 1972) have indicated that in many cases such clouds are gravitationally unstable and undergoing collapse. This process is the accepted view of the formation of young star clusters and planetary systems. During the collapse phase high temperatures and pressures occur, densities from $10^{10} - 10^{16}/cm^3$ and temperatures to 2500K appear likely. As the infall of matter ceases, the cloud temperature falls and the cloud becomes much colder again. It is during this latter stage that planet accumulation would primarily take place (Larimer, (1970); Anders (1971).

This paper considers chemical processes that could determine the molecular composition of the cloud during the several stages of its evolution. In particular we examine thermal reactions at the relatively high interstellar densities expected during the process

Three distinct circumstances occur to which our analysis applies.

1. The Origin of the Observed Molecules:

A. If the molecules preceded collapse and star formation, the molecule formation mechanism is very uncertain but thermal processes

are unlikely. However, there is a tendency for many of the observed polyatomic molecules in Orion to be concentrated in small regions associated with the infra-red source (Snyder and Buhl, 1971; Penzias et al., 1971, Barrett et al. 1971) . In a paper at this symposium, Martin and Downes (1972) presented evidence for several regions of star formation in Sag B2. These are associated with dense, high temperature ionized regions which act as continuum sources.

B. A possible source of the molecules in these complex cloud arrays is in expanding atmospheres of newly formed stars with subsequent ejection into the cloud. A combination of expansion and turbulence set up by the onset of radiation of hot OB stars may well be a mechanisms to spread the molecule through a large volume of the surrounding cloud. Shimizu (1972) and in this symposium has considered the atmospheres of newly formed stars as molecular sources and attempted to calculate the composition. In this hypothesis thermal reactions would be a major source of molecules. The question arises as to the molecular composition when the temperature and density become so low that reactions effectively cease.

2. Molecular Evolution During Collapse:

According to hypothesis 1B, few (if any) polyatomic molecules would be present in the cloud during·collapse. However, during the subsequent cooling stage, as temperatures drop from about 2000K and densities are high, thermal reactions must occur. The cooled nebula would have a complex composition. Several detailed equilibrium calculations have been made for the primordial solar nebula (e.g. Urey, 1952; Lord, 1965; Larimer, 1967; Lewis, 1972). Closely related to this process is the evolution of precollapse molecules

in hypothesis 1A. In this situation a complex array of molecules

react thermally during the heating phase. At temperatures of

2000K or above and densities of 10^{-3} to 1 atmospheres equilibrium

would be quickly established. As the cloud cooled, the composition

would continuously change. We inquire as to the composition to be

expected when the temperature has fallen to the value occurring

when, in the primordial solar nebula, the various condensation

and accumulation processes occurred (Anders, 1971). In particular,

we consider the validity of thermodynamic equilibrium calculations

of molecular composition.

3. The concentration role of organic molecules in planetary

    chemical evolution:

Although this aspect of molecular phenomena is some what removed

from the main argument of the conference, non-thermodynamic equili-

brium effects may be significant and some consideration will be given to it.

Pre-collapse molecules may not survive the high temperature stage

in their initial array but a different array should appear during

the cooling phase as outlined in 2. Pre-collapse molecules may not

exist but, as in hypothesis 1B, they arise in the primordial stellar

nebula following star formation. Under any circumstance it thus

appears that an array of organic compounds are present when planets

accumulate around newly formed stars. What happens when massive,

planetary objects form? At the final stage of accumulation the

s olid material will have accreted into a hierarchy of planetesimals

(Savronov, 1964, 1966). These would impact on cool planetary surfaces

causing local high temperatures but with rapid cooling. Organic

compounds may tend to be destroyed as Sagan (1965) suggested but
as in hypothesis 2, the composition of the vaporized constituents
after cooling may well contain a disequilibrium excess of organic
molecules. Oro's (1965) proposal for the initiation of biochemical
evolution may have considerable merit according to this analysis.

As a model for the astronomical aspects of the collapse we use
Cameron's (1972) recent analysis of the formation of the solar
system. A massive cloud collapses and fragments into units con-
taining up to ten of solar masses. The sun and planets form from
a two solar mass fragment. Within 1 AU of the sun the temperature
reaches about 2000K and cools with a time scale of ten years. At
10 AU the temperature is much less than a thousand degrees with a
cooling time of 100-1000 years.

II. CHEMICAL PROBLEMS

A. Theory

Molecular equilibrium calculations for cool stellar at-
mospheres, interstellar clouds, and primordial stellar and planetary
nebula have assumed thermodynamic equilibrium. For several reasons
the applicability of thermodynamic equilibrium to these objects is
open to question. (1) Variations in temperature and pressure will
invalidate such analyses if the time scale for attaining equilibrium
is of the order of, or less than the time scale for astronomical
changes. A determination of each time scale must be made. (2)
Equilibrium calculations only yield results for those species that
are initially included in the program. It does not predict species.
Unexpected or non-equilibrium species regardless of concentration

would not appear in the results nor would their absence cause any obvious effects.

In order to investigate the question of the rate of approach to equilibrium and the ultimate molecular composition we have begun a series of experiments at high temperatures. Because of the continuously changing temperature and pressure, equilibrium, will not be attained in most cases except perphaps at the highest temperatures. An extremely·complex set of reactions would determine the composition at each stage. As the temperature decreases during the cooling phase, each reaction and molecular species will behave differently. Chemical processes will be frozen out and metastable products will tend to be preserved. Because of these problems with a theoretical calculation, this experimental study was begun. This procedure develops its own set of difficulties which must be overcome. Experimental techniques are being developed to accomplish this.

The first series of experiments are designed to determine the reaction rate as time scale for approach to equilibrium and its temperature dependence. The measurement of an overall activation energy will permit extrapolation of the reaction rates to lower temperatures where rates are too slow for experimental determination.

B. Experiments

Mixtures of HCN and H_2 in ratios of 1:100, 1:000, 1:3000 were prepared and heated in quartz reaction vessels at 1093K for various times. The starting pressure at room temperature was approximately 300 torr. At the operating temperature, the pressure in the vessel was about 1.3 atmospheres. As the final composition

did not noticeably depend upon the $NCN:H_2$ ratio, the experiments were run at the 1:100 ratio to enhance product yield and improve the accuracy of the results. After the nominal duration of heating the furnace was turned off and allowed to cool. The gradual cooling process had a significant effect on the shortest (2 hour) heating time only.

The fraction of HCN remaining is a measure of the completion of the reaction. Equilibrium calculations (Tsuji, 1964) show that at equilibrium the residual HCN concentration would be 0.1% at 1090K and 0.6° at 1170K. Figure 1 shows the residual HCN percentage as a function of heating time. From Figure 1, we obtain a half life (e^{-1}) of 18 hours. $HCN:H_2 = 1:100$ mixtures were also reacted at 1170K and 980 K. The decay times are listed in Table 2 for the three temperatures. The effective activation energy for the reaction, obtained from the dependence of reaction rate on temperature, is 20-25 k cal/mole. A value this low is unexpected as activation energies for reactions of stable molecules of this type generally fall between 40-100 k cal/mole (Bahn, 1968; Kondratiev, 1972).

A few runs were made with an oxygen or water concentration equal to that of hydrogen cyanide in the mixture. The essential result, the HCN decay time, was similar to the previous case.

There is a possibility that surface reactions made a significant contribution to the observed rate. A quartz vessel was filled with 20 quartz tubes, thereby increasing the surface to volume ratio by a factor of 9. In 2 10-1/2 hours, the $HCN:H_2$ mixture at 1090K showed a 2% HCN residue whereas from Figure 1, the anticipated residue was 55%. This indicates a major surface

reaction contribution which would explain the low activation energy derived from the experiment. It also means that the 18 hr half half-life is a lower limit.

An additional factor affecting the experiment is contamination by gases driven from the walls of the reaction vessel at the temperatures of 1000K over several hours. Significant hydrogen loss via diffusion through the walls occurs as well. For example, in forty eight hours 20 percent of the hydrogen was lost.

Work on these high temperature reactions related to molecular equilibrium in astrophysical systems is continuing in order to refine the experiments and extend the results to more systems and conditions.

C. Application to Cloud Equilibrium

We return to the question of the approach to thermodynamic equilibrium in a collapsing or cooling cloud or in an expanding stellar atmosphere or shell. Hydrogen cyanide is one of the more abundant interstellar molecules and also is an important reactive precursor in biochemical evolution (Calvin, 1969). Consequently the behavior of this compound not only gives some indication of the approach to equilibrium in a cloud but also yields information on the ultimate concentration of an important prebiotic specie.

The dependence of the rate of the HCN-H on surface to volume ratio indicates that the experimental half-life of 18 hr at 1090K is a lower limit. In table 2 we use this value and extrapolate to lower temperatures using activation energies of 20 and 50 kcal/mole. The higher value yields results that may be more applicable in the absence of extensive surface reaction. Further experiments will seek to establish the gas phase activation energy.

Table 3 shows that if the effective activation energy were as low as 20 kcal/mole, equilibrium would take approximately 300 years at 500K. In Cameron's latest model of the solar nebula this temperature is reached between 5 and 10 A.U. His calculated lifetimes are comparable to the chemical lifetime raising a question of the approach to thermodynamic equilibrium. Half lives calculated using an activation energy of 50 kcal/mole suggest that there would only be sufficient time to approach equilibrium within about one A.U.

In expanding atmospheres of red giant stars or in proto-stars the astronomical time scale is days or months. The present analysis indicates temperatures close to 1000K would be required to attain a close approach to equilibrium.

Reactions caused by impact of planetesimals on the earth's surface near the end of its accumulation are very complex to analyze. The rapid change in temperature and pressure in the vapor suggest an extremely non-equilibrium final composition. The present experiments give some support to the idea that organic compounds may have been present on the surface of the newly-formed earth.

There is some observational evidence that suggest organic compounds were present when objects accumulated in the solar nebula. A number of carbon radicals, CH, CN, C_2 and C_3, occur in cometary atmospheres. More complex parent compounds were almost certainly present in the primordial nebula from which comets accreted. If not originally present in the inner region, molecules like HCN could have formed in the non-equilibrium impact reactions.

The chemical theory and experiments are preliminary and the astronomical models are also very uncertain. Hence, no definite

conclusions can be reached. The present analysis does point out that non-equilibrium processes may become very important in determining the molecular composition of cosmic clouds. This possibility must be taken into account in drawing conclusions from calculated compositions.

A continuing study of this problem is under way. We will investigate more thoroughly the limits of validity of thermodynamic equilibrium in the astronomical systems considered here. Procedures for estimating molecular compositions when thermodynamic equilibrium do   not apply are also being examined.

REFERENCES

Anders, E. (1971) Ann. Rev. Ast. Astrophys. $\underline{9}$, 1.

Bohn, G. S. (1968) Reaction Rate Compilation for the H-O-H Syste,
    Gordon and Reach, N.Y.

Barrett, A. H., R. P. Schwartz and J. W. Waters (1971) Ap. J. $\underline{168}$, L101.

Calvin, M. (1968), Chemical Evolution Oxford University Press, N. Y.

Cameron, A.G.W. (1969) In "Low Luminosity Stars" ed. by S. S. Kumar,
    Gordon and Beach, N. Y.

Cameron, A.G.W. (1972) Preprint submitted to ICARUS.

Kaplan, S. A. and S. B. Pilelner (1970) The Interstellar Medium, Harvard
    Univ. Press, Cambridge, Mass. 1970.

Kondratiev, V. N. (1972) Rate Constants of Gas Phase Reactions- Reference
    Book trans. L. J. Holtschlag ed. R.M. Fiestrom, Office Standard
    Reference Data, N.B.S , National Technical Information Service,
    Washington, D.C. USA.

Larimer, J. W. 1967 Geochim et Cosmochin Ortec 31, 1215.

Lewis, J. S. (1972) Iscarus $\underline{16}$, 241.

Liege Astrophysics Symposium (1970) Stellar Evolution before the Main
    Sequence, see particularly introductory reports and references,
    Univ. of Liege, 1970.

Lord, H. C. (1965) Icarus, 4, 279.

Oro, J. (1965) In "The Origin of Prebiological Systems" ed by S. W. Fox,
    p. 137, Academic Press, N. Y.

Penzias, A. A., P. M. Solomon, R. W. Wilson, and K. B. Jefferts (1971)
    Ap. J. $\underline{168}$, L. 53.

Sagan, C. (1965) In "The Origin of Prebiological Systems" ed. by

    S. W. Fox, see discussion following paper by Oro, p. 102,

    Academic Press, N. Y.

Savronov, V. S. (1964) Techtonophysics $\underline{1}$, 217.

Savronov, V. S. (1966) Sov. Ast. A. J. (Eng. Tran.) 9, 987.

Shimizu, M. (1972) Prog. Theoretical Physics,in Press.

Snyder, L. E. and D. Buhl (1971) Ap. J. 163, L47.

Tsuji, T, (1964) Ann. Tokyo Ast. Obs. $\underline{9}$, 1.

Urey, H. C. (1952) The Planets, Yale Univ. Press, New York.

TABLE 1

Half Life of $HCN-H_2$ Reaction (Measured)

T	$\tau(e^-)$ hrs.
1170	9
1093	18
980	53

TABLE 2

Half Life of $HCN-H_2$ Reaction (Theory)

Activation Energy

$T(^{\circ}K)$	E - 20 kcal/mole	E - 50 kcal/mole
2000	0.27 hrs	2 sec
1500	1.48 hrs	140 sec
1000	40 hrs	147 hrs
900	120 hrs	101 hrs
800	20 days	94 days
700	123 days	7.2×10^3 years
500	270 yrs	1×10^9 years

Figure 1: Dependence of HCN-H$_2$ reaction on time. The
dashed vertical bar at 100 hrs. is the un-
certainty of measuring that quantity of HCN
on the mass spectrometer.